Research Article

Hierarchization of Physicochemical Factors during Simultaneous Removal of Lead and Copper from the Marrakech Municipal Discharge Soils

Abdelaaziz Aityoub [1,2] **Abdessalem Abouelfida,**[1] **Abdelaziz Benyaich** [1] **Mohamed Elmeray,**[1] **Rachid Idouhli** [1] **Yassine Koumya** [1] **and Mohyeddine Khadiri**[1]

[1]*Laboratory of Physico-Chemistry of Materials & Environment (LPCME), Department of Chemistry, Faculty of Sciences Semlalia, Cadi Ayyad University, Marrakech, Morocco*
[2]*Ecole Normale Superieure, Department of Chemistry, Cadi Ayyad University, Marrakech, Morocco*

Correspondence should be addressed to Abdelaaziz Aityoub; aziz.ayoub@gmail.com

Heavy metals became a great concern for scientists due to their harmful action on the environment and human life. EDTA and NTA chelation capacity were used to assess soil decontamination. The effect of pH, ligand, soil solution contact time with agitation, soil solution ratio, and particle size were investigated, in order to prioritize them, using the design of experiment methodology (Doe): pH was the most influential factor while the ratio mass of the soil by the volume of the solution and particle size were of equal importance. EDTA was more effective as a chelator than NTA in removing metals from the soil. The contact time was not a significant factor; a contact time of 10 minutes was sufficient to extract the two metals studied. An extraction efficiency of 45% was achieved for Pb and 85% for Cu without optimization process.

1. Introduction

Over the centuries, human activities have contaminated large areas in both developed and developing countries. An example of these areas is the city of Marrakech in the Kingdom of Morocco. The commercial and industrial activities of Marrakech promote the economy of the region but also generate many environmental problems. One of them is clearly the management of waste and residues from these different activities. The collection and burial activities of the Marrakech municipal waste dump play an essential role in the management of garbage in the province, but, on the other hand, they generate other problems, such as the management of soil, aquifer resources, and local flora and fauna contamination. Contaminants can be of two kinds: organic or inorganic. Organic contaminants, whose presence is mainly due to human activity, can be toxic and even carcinogenic [1]; they are issued from petroleum hydrocarbons, solvents, pesticides, etc. Inorganic contaminants are mainly metals (Cu, Fe, Ni, Zn, . . .) and metalloids (As, B, Te, . . .) found naturally in the Earth's crust but the anthropogenic human activities cause these metals to accumulate on sites well beyond the concentrations inherited from the parent rock [2, 3]. Sometimes the concentrations are so high that they represent a danger to the fauna, flora, and human health. Heavy metals constitute a major factor of this pollution due to their atmospheric deposition, their leaching tendency, and the fact that they are nondegradable, unlike organic compounds. The cleanup usually requires their removal. Several decontamination techniques have been developed in research laboratories and industrial sites in order to eradicate this pollution or at least to minimize its effects. For example, we can cite electroplating [4], electrocoagulation [5], phytoremediation [6], extraction by adsorption [7], and extraction by organic complexing agents [8, 9].

Among the remediation techniques for soil contaminated with heavy metals, washing has given very interesting results. Various extraction agents have been used in the washing of soils such as acids, bases, surfactants, and complexing agents. Some of these extractants destroy the structure of the soil. Yobouet et al. reported that the use of HCl at pH = 0.5 dissolves all the nonresidual soil's fractions and a part of the residual one [10]. This is not the case with complexing agents such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) which are powerful enough to efficiently extract the heavy metals retained in different fractions of the soil while preserving their consistency. Although less effective than EDTA, NTA is a more readily biodegradable reagent [11].

Two representatives of heavy metals were included in the study: Pb and Cu. The micronutrient Cu, called protective food, is necessary for life and represents a danger only beyond a certain limit defined by the World Health Organization (WHO) among other institutions [12, 13]. On the other hand, Pb has no role in the physiological activity of animals or plants and constitutes a danger to human health [12, 14].

EDTA and NTA, Like a lot of other chelants, have already been studied for their extracting power of metals from the soil [9, 15, 16] and for their capability to increase the dissolution and availability of heavy metals during phytoremediation and soil wash [16, 17]. This extraction is determined by the physicochemical parameters of the soil-chelate system. Several parameters can influence the removal of heavy metals from the soil. We can mention pH, ligand, concentration, temperature, nature of the soil [18], etc. Our objective was to establish a hierarchy of physicochemical factors controlling the extraction efficiency of Cu and Pb from the soil of the municipal landfill of Marrakech by the use of two organic chelants, EDTA and NTA. We aimed also to study the interactions between these factors (synergistic or inhibitory) and finally to propose a modeling of this extraction according to factors. They are nature of the chelating agent [19], pH of the medium, the ratio mass of the soil to volume of the extractant solution [20], soil's particle size [21], and the contact time between the soil and the extracting's solution [18].

The experimental methodology was adopted to achieve these objectives: a fractional factorial design $2^{(5-1)}$ was used to determine the effects of the five factors studied on the extraction and the intensity and the type of interactions between them [22].

2. Material and Methods

2.1. Samples Preparation.
The soil studied consists of a mixture of several samples collected from depths up to 30 cm, from different locations in and around the Marrakech municipal landfill. Once dried in open air and under shade, the samples were sieved to 2 mm. After physicochemical characterization, they were separated into two fractions: the first one called fine and designated by (F) with particle diameter less than or equal to 1 mm, and the second called coarse and designated by (C) consisting of particles having a diameter between 1 and 2 mm. They were then stored in propylene jars until use.

2.2. Chemicals Preparation.
The EDTA solutions were prepared from the ethylenediaminetetraacetate disodium salt delivered by Ferak GmbH Laboratory; for the NTA solution, the nitrilotriacetic acid, provided by Sigma Aldrich Company, was used. The solutions of the two ligands were prepared by dissolving the appropriate masses in bidistilled water. To promote the dissolution, a few crystals of sodium hydroxide have been added to increase the pH to alkaline value [23]. The solutions were then sealed and stored at 4°C until use. All reagents were of analytical grade.

2.3. Total Metal.
To determine the metal content in the two classes of samples, acid digestion of 1.0 g of soil dry sample was carried out with a mixture of acids as follows [24, 25]:

(i) The sample was mixed with 2 ml of $HClO_4$ and 10 ml of HF and then heated to dryness.

(ii) Then, the precipitate was dissolved with 1 ml of $HClO_4$ and 10 ml of HF and heated until almost total evaporation of the liquids.

(iii) Finally, 1 ml of $HClO_4$ was added and the liquids were evaporated until white fumes appeared.

The solid was dissolved with 12N HCl and diluted to 25 mL. The solution was then stored in a tightly closed propylene jar and stored at 4°C until analyses, which were carried out by inductively coupled plasma atomic emission spectroscopy (AES-ICP).

2.4. Extraction.
To extract heavy metals from soil samples, two ligands' aqueous solution $c = 0.01 \, mol \, L^{-1}$ was used [9]: EDTA and NTA. The first is a relatively strong chelator [23, 26]; however it presents a risk of toxicity [23]. The second is biodegradable [27, 28] and has a structure similar to EDTA [29] and, therefore, a comparable chelating tendency. The value of the concentration was chosen taking into consideration two criteria: the ligand should be in excess of the different metal ions present in the medium, and according to the literature the optimal concentration is about $0.01 \, mol \, L^{-1}$ [18, 23, 30, 31].

A mass m (1 or 5 g) of the fraction considered (F or C) was weighed and mixed with 20 mL of the solution, $c = 0.01 \, mol \, L^{-1}$, of the ligand (EDTA or NTA). The pH was adjusted to the desired value with molar solution of hydrochloric acid HCl and sodium hydroxide NaOH during stirring (240 rpm) time T (10 or 60 min), following the experimental design as shown in Table 1.

Once the time T has been consumed, the mixture was centrifuged at 2000 rpm for 10 minutes, and then the supernatant was filtered, acidified with a 10% nitric acid solution, and stored at the temperature of 4°C until its analysis by AES-ICP.

TABLE 1: Experimental design and the responses Y_{Pb} and Y_{Cu}.

No exp	Randomized order	Experimental conditions					Experimental design					Responses	
		Ligand	pH	m(g)/V (20 mL)	Size	Time (min) min	X1	X2	X3	X4	X5	Y_{Pb} (%)	Y_{Cu} (%)
1	2	EDTA	2	1	F	60	−1	−1	−1	−1	1	39.231	72.185
2	3	EDTA	2	1	F	60	−1	−1	−1	−1	1	45.868	76.744
3	16	NTA	2	1	F	10	1	−1	−1	−1	−1	32.676	62.156
4	14	NTA	2	1	F	10	1	−1	−1	−1	−1	31.873	62.298
5	25	EDTA	10	1	F	10	−1	1	−1	−1	−1	17.485	23.652
6	17	EDTA	10	1	F	10	−1	1	−1	−1	−1	16.570	26.506
7	24	NTA	10	1	F	60	1	1	−1	−1	1	2.518	14.758
8	13	NTA	10	1	F	60	1	1	−1	−1	1	0.967	16.101
9	21	EDTA	2	5	F	10	−1	−1	1	−1	−1	40.941	53.234
10	9	EDTA	2	5	F	10	−1	−1	1	−1	−1	29.151	51.760
11	22	NTA	2	5	F	60	1	−1	1	−1	1	17.913	42.676
12	10	NTA	2	5	F	60	1	−1	1	−1	1	12.180	36.231
13	6	EDTA	10	5	F	60	−1	1	1	−1	1	9.115	13.716
14	19	EDTA	10	5	F	60	−1	1	1	−1	1	10.452	6.657
15	8	NTA	10	5	F	10	1	1	1	−1	−1	1.757	1.018
16	27	NTA	10	5	F	10	1	1	1	−1	−1	1.327	4.763
17	7	EDTA	2	1	C	10	−1	−1	−1	1	−1	24.863	71.805
18	18	EDTA	2	1	C	10	−1	−1	−1	1	−1	39.012	110.013
19	4	NTA	2	1	C	60	1	−1	−1	1	1	29.990	85.508
20	26	NTA	2	1	C	60	1	−1	−1	1	1	33.547	81.840
21	30	EDTA	10	1	C	60	−1	1	−1	1	1	3.946	14.712
22	11	EDTA	10	1	C	60	−1	1	−1	1	1	4.459	11.787
23	1	NTA	10	1	C	10	1	1	−1	1	−1	3.573	8.997
24	12	NTA	10	1	C	10	1	1	−1	1	−1	3.573	13.612
25	15	EDTA	2	5	C	60	−1	−1	1	1	1	26.547	37.730
26	20	EDTA	2	5	C	60	−1	−1	1	1	1	24.685	34.865
27	23	NTA	2	5	C	10	1	−1	1	1	−1	14.125	31.171
28	5	NTA	2	5	C	10	1	−1	1	1	−1	15.810	35.279
29	28	EDTA	10	5	C	10	−1	1	1	1	−1	0.274	7.329
30	32	EDTA	10	5	C	10	−1	1	1	1	−1	0.125	3.916
31	31	NTA	10	5	C	60	1	1	1	1	1	1.087	1.662
32	29	NTA	10	5	C	60	1	1	1	1	1	2.663	3.480

2.5. Factors' Effects Measurement.

The effect, on the efficiency of extraction, was investigated for the five factors [18, 32] (Table 2).

A two-level fractional factorial 2^{5-1} design [33, 34] was adopted to evaluate the effect of these factors on the extraction process and to estimate the interactions between them. Each factor was associated with a coded variable Xi (centered and normalized) defined as follows [34].

$$X_i = \frac{U_i - ((U_{i\max} + U_{i\min})/2)}{((U_{i\max} - U_{i\min})/2)} \quad (1)$$

The goal was to determine the response's coefficients of a first-degree model Y_M (2) valid only for $X_i = +1$ and $X_i = -1$:

$$Y_M = b0 + b1 \times X1 + b2 \times X2 + b3 \times X3 + b4 \times X4 + b5$$
$$\times X5 + b12 \times (X1 \times X2) + b13 \times (X1 \times X3) + b23$$
$$\times (X2 \times X3) + b14 \times (X1 \times X4) + b24 \times (X2 \times X4)$$
$$+ b34 \times (X3 \times X4) + b15 \times (X1 \times X5) + b25$$
$$\times (X2 \times X5) + b35 \times (X3 \times X5) + b45 \times (X4 \times X5),$$
$$(2)$$

TABLE 2: The five factors' experimental field and associated coded variables.

Factor	Coded variable	Number of levels	Level	
			Low	High
Ligand	X1	2	EDTA	NTA
pH	X2	2	2	10
m/V (g/20 mL)	X3	2	1	5
Size	X4	2	F	C
Time (min)	X5	2	10	60

where

(i) M was the considered metal.

(ii) Y_M was the efficiency of the metal's extraction defined as follows:

$$Y_M (\%) = 100 \times \frac{C_{\text{extraite}} (\text{mg/kg})}{C_{\text{metal total}} (\text{mg/kg})}. \quad (3)$$

(iii) C_{extraite} (mg/kg) was the concentration of the metal in the extract.

(iv) $C_{\text{metal total}}$ (mg/kg) was the total concentration of the metal in the soil.

In addition, the other coefficients are described in Table 3.

Repetitions were performed to estimate accuracy and deviations. The 2^{5-1} factorial fractional experimental design, as generated by NEMRODW software, was reported in Table 1. The experiments were conducted in a randomized order; thus uncontrollable factors would not influence the results.

3. Results and Discussion

3.1. Sample Characterization.
The physicochemical properties of the samples are listed in Table 4.

The total metal content is shown in Table 5.

The samples were of slightly alkaline pH. The pH in the presence of KCl was slightly lower than that in water. This was explained by the displacement of acidic cations from the soil to the solution by the K^+ cations. In these conditions, the leaching of heavy metals by rainwater will be limited. The presence of organic matter suggested that the soil could potentially have a heavy metal retention property [37].

The total concentration of Pb was 53.8 ppm. It was beyond the RV (twice as large) without exceeding the VS.

For Cu the total concentration, 11.3 ppm, in the soil of the discharge was equal to the RV. As shown in Table 6, the total Cu content was the same in fraction F and C of the soil. Pb was more present in the fine fraction than in the coarse one. In order to determine the classification of the effects of factors on the extraction of metals from the soil, we preferred to work on samples with a low content of heavy metals. We thus hoped to increase the sensitivity of our tests. Thus, in future attempts at decontamination, we will probably act on the most determining factors for an optimal result.

3.2. Metal Removal Study.
The removal efficiency Y_M, as shown in Table 1, varied from 0.125% to 45% for Pb and from 1% to 85% for Cu depending on experimental conditions. The factors actually played a very important role. Indeed, the modification of the experimental conditions changed the extraction efficiency by a factor greater than 80 for both metals.

The coefficients as computed by NEMRODW software, based on the result of the 32 experiments of the experimental design, are given in Table 7 bellow with the corresponding p factor (significance %).

Hence, the Pb extraction efficiency was expressed in (4) by the following.

$$
\begin{aligned}
Y_{\text{Pb}} \text{ computed} = {} & 16.82 + (-3.97) \times X1 + (-11.83) \times X2 + (-3.81) \times X3 + (-2.55) \times X4 + (-0.25) \times X5 + 1.16 \times (X1 \times X2) \\
& + (-0.68) \times (X1 \times X3) + 2.17 \times (X2 \times X3) + 2.75 \,(X1 \times X4) + 0.02 \,(X2 \times X4) + 0.21 \times (X3 \times X4) + 0.01 \\
& \times (X1 \times X5) + (-0.34) \times (X2 \times X5) + 0.32 \times (X3 \times X5) + 1.85 \times (X4 \times X5).
\end{aligned}
$$

$$(4)$$

For Cu the efficiency of extraction was also given in (5) as follows.

$$
\begin{aligned}
Y_{\text{Cu}} \text{(computed)} = {} & 34.94 + (-3.60) \times X1 + (-24.15) \times X2 + (-12.10) \times X3 + (-0.34) \times X4 + (-0.53) \times X5 + 0.85 \\
& \times (X1 \times X2) + 0.29 \times (X1 \times X3) + 6.63 \times (X2 \times X3) + 1.68 \times (X1 \times X4) + (-2.27) \times (X2 \times X4) + (-3.08) \\
& \times (X3 \times X4) + 4.46 \times (X1 \times X5) + 0.09 \times (X2 \times X5) + (-0.19) \times (X3 \times X5) + (-0.13) \times (X4 \times X5).
\end{aligned}
$$

$$(5)$$

However, only the factors and interactions including the factor $p \leq 5\%$ are determining factors. They were indicated, in Table 7, by a *, **, or *** in the column giving the values of p.

3.3. Factors Effect.
The analysis of the results revealed that only pH ($b_2 = -24.15$), m/V ($b_2 = -12.1$), and ligand nature ($b_1 = -3.6$) were decisive factors for the extraction of Cu. For Pb extraction, the decisive factors were pH ($b_2 = -11.83$), ligand nature ($b_1 = -3.97$), m/V ($b_3 = -3.81$), and particle size ($b_4 = -2.55$). As expected pH was the most influential factor for both metals. Only Pb extraction was influenced by particle size. All the statistically significant effects have a negative coefficient: the decrease of those values increased the removal efficiency of the two metals from the soil.

3.4. The Interactions.
We could not conclude on the effect of the different factors on the metals removal without taking into account the interactions between them. The different factors interacted positively or negatively and therefore determined the efficiency of the extraction. These interactions would favor the effect of factors when they are constructive (positive coefficient) or attenuate them when they are destructive (negative coefficient). Only the interactions between the significant factors were taken into account.

For Cu the pH/m/V ratio interaction was the only one to meet this requirement. They interacted positively ($b_{23} = 6.62$). As revealed in Figure 1, at pH = 10 the decrease of the ratio m/V increased the efficiency tree time but it remained low (16%). On the other hand at pH = 2, the variation was less important (two times) but the removal

TABLE 3: The Y_i coefficients meaning [35].

Coefficient	Name	Signification
b0	Constant	The average value
bi	Coefficient of X_i	Linear effect of the associated factor
bij	Interaction coefficient between X_i and X_j	Interaction between associated factors

TABLE 4: Physicochemical value summary.

	pH (H$_2$O)	pH (KCl)	G (mS)	τ_{hum} (%)	% mo
Max	8.16	8.08	0.535	3.06	4.95
Min	7.6	7.12	0.502	2.77	3.87
Average	7.89	7.61	0.525	2.96	4.02

TABLE 5: Metal total content and referential values.

Metal	Cu (mg/kg)	Pb (mg/kg)
Min	11.80	43.96
Max	10.92	63.62
Average	11.36	53.79
RV [36]	14	25
VS [36]	50	200
VI [36]	145	400

For natural and agricultural soil, RV: reference value, an average natural value of metal concentration in soil as inherited from the mother rock; VS: threshold value, value of metal concentration beyond which studies must be conducted; VI: intervention value; if this value is exceeded, remediation measures must be taken.

TABLE 6: Metal total content in F and C fractions.

MT mg/kg	Cu (mg/kg)	Pb (mg/kg)
C	11.2	48.1
F	10.5	61.7

efficiency reached 77.8%. The removal efficiency was maximal when pH and the ratio m/V were both at low level.

For Pb removal, the statistically significant interactions between factors were in decreasing order as shown in (Table 7): ligand/particle size ($b_{14} = 2.75$), pH/m/V ($b_{23} = 2.17$), and particle size/contact time ($b_{45} = 1.85$).

The other interactions were statistically insignificant: the p factor was greater than 5%. The interaction between particle size and contact time (b_{45}) involved no significant factor (contact time). The most significant was that between ligand and soil particle's size ($b_{14} = 2.75$). As shown in Figure 2 the extraction efficiency, when using NTA as chelator, did not vary with particle size ($Y_{Pb} = 13\%$). However, with EDTA the Pb removal efficiency was better with particles of small size. The maximum ($Y_{Pb} = 26\%$) was reached when both factors were in their low level: EDTA as ligand and soil particle's size <1 mm.

In the second place came the interaction between the two factors pH and the ratio of soil mass to the volume of the chelator solution. As shown in Figure 3 the decrease of the ratio m/V increased the Pb removal amount. The variation was more important at pH = 2 than at pH = 10.

Given the above, we have adjusted the expression of the metal M removal efficiency Y_M (computed) as Y_M (adjusted) expressed in (6) and (7).

$$Y_{Cu} \text{ (adjusted)} = 34.94 + (-3.60) \times X1 + (-24.15) \times X2 \\ + (-12.10) \times X3 + 6.62 \times (X2 \times X3). \tag{6}$$

$$Y_{Pb} \text{ (adjusted)} = 16.82 + (-3.97) \times X1 + (-11.83) \times X2 \\ + (-3.81) \times X3 + (-2.55) \times X4 + 2.17 \\ \times (X2 \times X3) + 2.75 \times (X1 \times X4). \tag{7}$$

The two functions Y_{Cu} (adjusted) and Y_{Pb} (adjusted), although simplified, enabled us to find the values measured experimentally as shown by the two graphs Y_{Cu} (adjusted) = f (Y_{Cu} (experimental)) and Y_{Pb} (adjusted) = f (Y_{Pb} (experimental)) in Figure 4. Correlation coefficients R and standard deviation SD are given in Table 8.

Although simpler, both expressions contain all the information relating to the variation of the efficiency of extraction of the corresponding metal according to the different factors. Indeed the corresponding correlation coefficient, between the experimental removal efficiency and the calculated one, is 0.961 and 0,968, respectively, for Cu and Pb as shown in Table 8.

3.5. Effect of Ligand. The extraction with chelating agents aimed to measure the mobilizable metal fraction, that is to say, the active part of the pollution and a potentially active part that could be available depending on the physicochemical conditions. EDTA, like NTA, is a complexing agent strong enough to extract metals related to different soil's fractions (soluble, bound to carbonates, bound to oxide, and a part of the metal bound to organic matter) except the metal fraction bound to silica [38]. EDTA is a hexadentate chelating agent while NTA is tetradentate one. EDTA turned out to be better than NTA for the extraction of both metals ($b_1 = -3.6$ for Cu and -3.81 for Pb). This was in agreement with the values of the formation constants of the considered chelates (K_f $_{CuEDTA} = 20.6$, K_f $_{PbEDTA} = 19.7$, K_f $_{CuNTA} = 13.05$, and K_f $_{PbNTA} = 11.4$) [39–41]. However, the extraction of Cu was not affected by the choice of the ligand ($b_1 = -3.6$) which came in the third position relative to the pH ($b_2 = -24.15$) and the m/V ratio ($b_3 = -12.1$). On the contrary, the extraction of Pb depended on the nature of the ligand as shown in Figure 2. It was, like the ratio m/V, the second important factor after pH. This suggested that the efficiency of Cu extraction depends on the amount of ligand and the amount of Cu in soil solution. On the other hand, for

TABLE 7: The Y_{Cu} and Y_{Pb} coefficients and their statistical significance.

Coefficients	Y_{Cu} coefficients	p factor (%) [1]	Y_{Pb} coefficients	p factor (%) [1]
b0	34.94	<0.01***	16.82	<0.01***
b1	−3.6	1.23*	−3.97	<0.01***
b2	−24.15	<0.01***	−11.83	<0.01***
b3	−12.1	<0.01***	−3.81	<0.01***
b4	−0.34	79.2	−2.55	0.139**
b5	−0.53	68.8	−0.25	71.1
b12	0.85	52.2	1.16	9.3
b13	0.29	82	−0.68	31.9
b23	6.63	0.0113***	2.17	0.454**
b14	1.68	20.5	2.75	0.0762***
b24	−2.27	9.2	0.02	97
b34	−3.08	2.76*	0.21	75.2
b15	4.46	0.311**	0.01	98.7
b25	0.09	94	−0.34	61.4
b35	−0.19	87.9	0.32	63.8
b45	−0.13	91.6	1.85	1.23*

[1]Any parameter is statistically significant if the corresponding p is less than or equal to 5%.
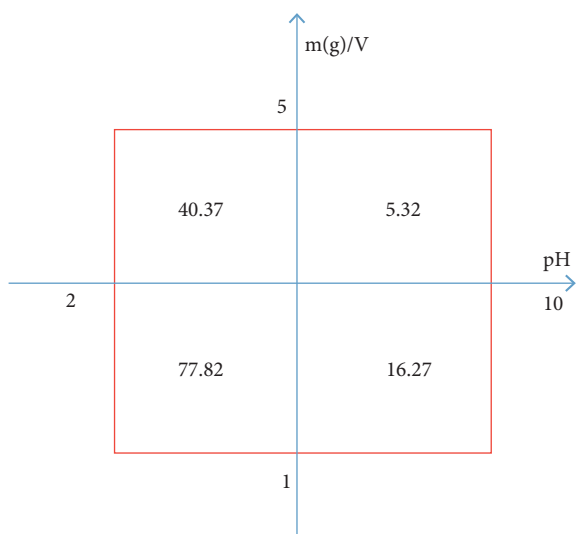
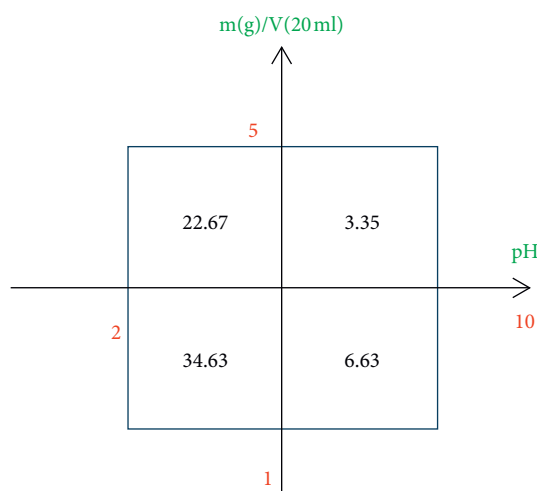FIGURE 1: Y_{Cu} as function of pH and m/V interaction.

FIGURE 2: Ligand and particle size interaction diagram for Pb extraction.

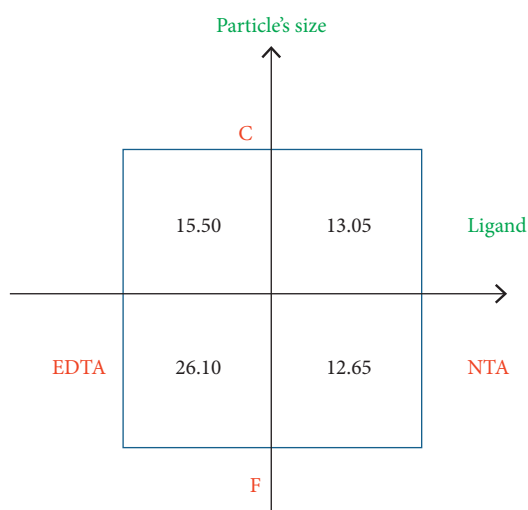FIGURE 3: pH and the ratio of soil mass to the volume of the chelator solution interaction diagram for Pb extraction.

Pb, the metal-soil interaction and metal-ligand interaction were also decisive; there must be interference with the other constituents of the system. Labonowski et al [42] suggested that Cu had a more homogeneous binding strengths (with one or more soil constituents) compared to Pb. Cu was reported to be mainly retained in the organic and residual fraction of the soil and consequently it was strongly and uniformly bound to the soil. The Pb was bound to different soil's fractions and consequently it presented different behaviors according to the strength of its connection to the concerned fraction.

3.6. Effect of pH. As expected, according to literature, pH was the most influential factor on the removal of both metals ($b_2 = -24.15$ for Cu and -11.83 for Pb) and the extraction efficiency was increased in acidic medium. This was in accord with the fact that the soil dissolution was promoted at low pH and hence the metallic ions became available in
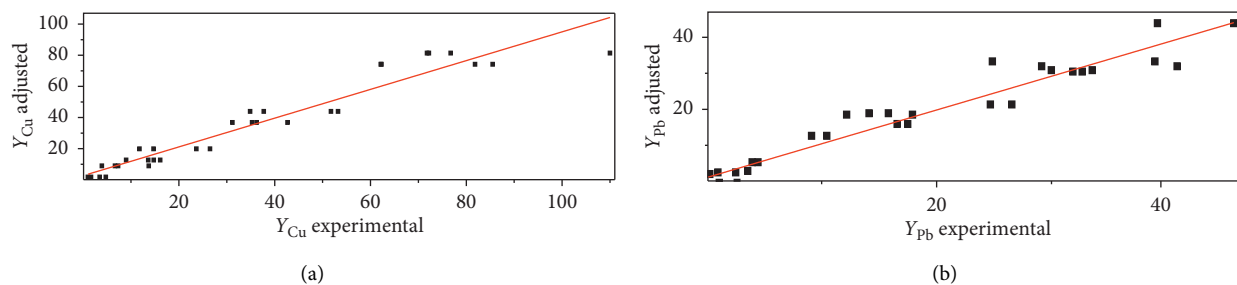
(a)

(b)

FIGURE 4: Correlation between model Y_M (adjusted) and experimental data Y_M.

TABLE 8: Correlation coefficient and standard deviation for Y_M (adjusted) $= f$ (Y_M (experimental)).

Y_{Cu} (adjusted)		Y_{Pb} (adjusted)	
R	SD	R	SD
0,961	7,99	0,968	3,53

solution. An acidic pH leads to the dissolution of the metal salts, the dissolution of the retention phases, the cations' desorption, and the anions' adsorption. The solubility therefore decreases when the pH increases, goes through a minimum, and then increases when the element may exist in anionic form.

EDTA like NTA is polyacid. EDTA is a tetraacid ($pK_{a1} = 2$, $pK_{a2} = 2.7$, $pK_{a3} = 6.2$, and $pK_{a4} = 12.4$). For NTA ($pK_{a1} = 1.9$, $pK_{a2} = 2.5$, and $pK_{a3} = 9.7$). Because of the presence of a basic nitrogen atom in both ligands' molecules, the sequestering tendency is strongly dependent on the pH value [39]. The chelator's capacity decreased in acidic medium. Zhang et al [18] showed that EDTA free acid was more efficient for metal removal than its disodium salt. There had to be a compromise: the study suggested that the dissolution of the soil matrix was more decisive than the variation in the capacity of the chelator with pH. Indeed, F. Smith [43] reported that in the presence of metal the two ligands were mainly in the form of their respective complexes.

3.7. Effect of Ratio m/V. This factor was the second important one after the pH for the removal of both metals. It is equal to the ratio of the mass of the soil by the volume of the ligand solution. The elimination efficiency was favored by a small ratio that signified an excessive quantity of the ligand compared to the metal ions; thus, the extraction was more efficient.

This factor had a more preponderant effect on the extraction of Cu than on that of Pb ($b_3 = -12.1$ for Cu and $b_3 = -3.81$ for Pb). This difference could not be attributed only to the difference between the stability constants of the metal EDTA and metal NTA complexes ($K_{f\ CuEDTA} = 20.6$, $K_{f\ PbEDTA} = 19.7$, $K_{f\ CuNTA} = 13.05$, and $K_{f\ PbNTA} = 11.4$) [39–41]. For Cu, as suggested by Andrade [44], its extraction was not limited by the soil's dissolution. The greater the quantity of ligand present, the greater the quantity of Cu extracted; this is the case when m/V is at its low level (m/V = 1/20). This was consistent with the fact that Cu is

homogeneously retained in the soil [42]. But Pb's extraction was limited by the soil retention and by the interference of other soil's constituents [45]. The amount of Pb extracted was not only a function of the amount of ligand present: there had to be other factors involved. As we had already reported, Pb was bound to different soil's fractions and consequently it showed different behaviors according to the strength of its connection to the concerned fraction. This could explain the difference in the effect of the factor m/V on the extraction efficiency of Cu and Pb.

3.8. Effect of Soil's Particle Size. The smaller the particle size of the soil, the greater the specific surface presented to the ligand. Thus, the ligand metal interaction is more effective because the latter is more accessible. Consequently, the quantity of metal potentially accessible by the ligand will be greater [46]. Cu extraction was not significantly influenced by the soil's particle size. This would suggest that the target portion of Cu was identically retained in the two fractions considered, F (for fine) and C (for coarse). Thus, the amount of Cu accessed by the ligand was controlled by the amount of ligand in solution (m/V factor) rather than by the soil's metal retention process. Pb was better extracted from the fine fraction than from the coarse one [47]. This suggested that it was more present in fine fractions (size <1 mm), as shown in Table 6 and proposed by many authors [46], and/or that it was more strongly retained in the coarse fraction (size >1 mm). Pb ions would not be readily available to the ligand as explained when discussing m/V effect: the chelator, EDTA or NTA, had to compete with the bonding strength of Pb to the soil and probably to the other constituents of the soil, in particular, organic matter [48]. As we have seen in Table 6, Pb was more present in the fine fraction than in the large fraction of the soil, and therefore it was more extracted from fraction F than from fraction C. This could explain the effect of the size of the soil particles on the extraction of Pb. On the other hand, Cu was distributed identically over the two fractions F and C, and therefore the effect of the size factor of the soil particles was insignificant during the Cu extraction. In summary, the effect of particle size reflected the distribution of metals on the two fractions F and C.

3.9. Effect of Contact Time. Time was a statistically insignificant factor on the extraction of both metals. Increasing the contact time between the ligand solution and the soil

from 10 to 60 minutes does not bring a significant gain in extraction efficiency. A 10-minute contact, while stirring at the speed of 240 rpm, between the soil and the ligand solution seemed sufficient to extract the two metals from the studied soil. During our preliminary tests, we worked with two contact durations of 1 and 10 hours. However, time was not a determining factor. We then chose to work with the two durations 10 and 60 minutes in the hope of having a significant contact time effect. This result did not mean that time had no effect on this extraction, but that its effect was much less significant than that of the four other factors studied. We suspected the existence of a competition between the phenomena of soil dissolution, metal complexation, and reprecipitation of the latter in other forms (carbonates, hydroxides, ...).

In summary, EDTA was a much more powerful chelator than NTA [42] as evidenced by the formation constants of the Cu and Pb complexes. The extraction of Pb by NTA was not affected by the particle size of the soil. However, the use of EDTA was sensitive to this factor. Being a powerful chelator, EDTA had access to fractions firmly linked to the soil. Consequently, the effect of the interface of the soil solution would be decisive: the smaller the size, the larger the interface and therefore the greater the amount of Pb extracted. Cu was a fairly mobile metal, so the quantity in solution will be relatively large, and therefore it would be available to be complexed by the ligand. Since mobility was highly dependent on pH, it had a much greater effect in the case of Cu ($b_2 = -24.18$) than in the case of Pb ($b_2 = -11.83$); thus, the greater the amount of ligand in the medium, the higher the efficiency of Cu extraction. A linear correlation between the quantity extracted and the quantity of ligand has been reported [44]. This was not the case for Pb for which the metal-soil bond strength determined the amount of metal extracted. The competition between the complexing capacity of the ligands (strong in their deprotonated form) and the dissolution of the soil in an acid medium was to the advantage of the pH. This was described by the pH-m/V interaction. The efficiency of Pb or Cu extraction was much greater at pH = 2 (protonated chelating form and maximum dissolution) than at pH = 10 (deprotonated ligand form and reduced dissolution).

4. Conclusions

In our study, we tried to classify the five factors studied according to the importance of their effect during the extraction of Cu and Pb. The pH was the most determining factor followed by m/V for Cu extraction and by m/V and ligand for Pb. The soil's particle size only influenced the extraction of Pb because it was more present in the fine fraction than in the coarse one. We could therefore ignore this effect on the extraction of Pb and Cu because it only reflected the distribution of the two metals in the soil fractions F and C. Among the five factors studied, the contact time, between the soil and the solution, was the least determining factor for the extraction efficiency of the two metals. The models represented by the two expressions Y_{Cu} (adjusted) and Y_{Pb} (adjusted) fairly well described the

experimental results as indicated by the values of the correlation coefficients R (0.961 for Cu and 0.968 for Pb). This comforted the choice of determining factors as being the statistically significant ones. An extraction efficiency of 45% was reached for Pb and 85% for Cu without optimization process.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

[1] C. Dassonville, C. Mandin, and S. Kirchner, "Pollutions à l'intérieur des espaces clos: sources, niveaux et impact sanitaire. Volet 2: polluants chimiques," *Archives des Maladies Professionnelles et de l'Environnement*, vol. 75, no. 6, pp. 594–606, 2014.

[2] P. J. C. Favas, J. Pratas, M. E. P. Gomes, and V. Cala, "Selective chemical extraction of heavy metals in tailings and soils contaminated by mining activity: environmental implications," *Journal of Geochemical Exploration*, vol. 111, no. 3, pp. 160–171, 2011.

[3] B. Suresh, G. Sudhakar, and T. Damodharan, "Determination of heavy metals in sugar industry effluent," *International Journal of Modern Engineering Research*, vol. 5, pp. 23–26, 2015.

[4] T. Panayotova, M. Dimova-Todorova, and I. Dobrevsky, "Purification and reuse of heavy metals containing wastewaters from electroplating plants," *Desalination*, vol. 206, no. 1-3, pp. 135–140, 2007.

[5] J. Lu, Y. Li, M. Yin, X. Ma, and S. Lin, "Removing heavy metal ions with continuous aluminum electrocoagulation: a study on back mixing and utilization rate of electro-generated Al ions," *Chemical Engineering Journal*, vol. 267, pp. 86–92, 2015.

[6] M. S. Sultana, Y. N. Jolly, S. Yeasmin, A. Islam, S. Satter, and S. M. Tareq, "Transfer of heavy metals and radionuclides from soil to vegetables and plants in Bangladesh," in *Soil Remediation and Plants*, pp. 331–366, Elsevier, Amsterdam, Netherlands, 2015.

[7] I. Sheet, A. Kabbani, and H. Holail, "Removal of heavy metals using nanostructured graphite oxide, silica nanoparticles and silica/ graphite oxide composite," *Energy Procedia*, vol. 50, pp. 130–138, 2014.

[8] T. Zhang, H. Wei, X.-H Yang et al., "Influence of the selective EDTA derivative phenyldiaminetetraacetic acid on the speciation and extraction of heavy metals from a contaminated soil," *Chemosphere*, vol. 109, pp. 1–6, 2014.

[9] R. W. Peters, "Chelant extraction of heavy metals from contaminated soils," *Journal of Hazardous Materials*, vol. 66, no. 1-2, pp. 151–210, 1999.

[10] A. Y. Yobouet, K. Adouby, A. Trokourey, and B. Yao, "Cadmium, copper, lead and zinc speciation in contaminated soils," *International Journal of Engineering, Science and Technology*, vol. 2, pp. 802–812, 2010.

[11] M. Bucheli-Witschel and T. Egli, "Environmental fate and microbial degradation of aminopolycarboxylic acids," *FEMS Microbiology Reviews*, vol. 25, no. 1, pp. 69–106, 2001.

[12] R. Egli, D. Hashim, D. R. Smith et al., "Metal contamination of home garden soils and cultivated vegetables in the province of Brescia, Italy: Implications for human exposure," *Science of the Total Environment*, vol. 518-519, pp. 507–517, 2015.

[13] T. Chen, X. Liu, M. Zhu et al., "Identification of trace element sources and associated risk assessment in vegetable soils of the urban-rural transitional area of Hangzhou, China," *Environmental Pollution*, vol. 151, no. 1, pp. 67–78, 2008.

[14] S. H. Xie, A. L. Liu, Y. Y. Chen et al., "DNA damage and oxidative stress in human liver cell L-02 caused by surface water extracts during drinking water treatment in a waterworks in China," *Environmental and Molecular Mutagenesis*, vol. 51, no. 3, pp. 229–235, 2010.

[15] O. Hanay, H. Hasar, and N. N. Kocer, "Effect of EDTA as washing solution on removing of heavy metals from sewage sludge by electrokinetic," *Journal of Hazardous Materials*, vol. 169, no. 1-3, pp. 703–710, 2009.

[16] E. V. d. S. Freitas and C. W. A. do Nascimento, "The use of NTA for lead phytoextraction from soil from a battery recycling site," *Journal of Hazardous Materials*, vol. 171, no. 1-3, pp. 833–837, 2009.

[17] J. Lan, S. Zhang, H. Lin et al., "Efficiency of biodegradable EDDS, NTA and APAM on enhancing the phytoextraction of cadmium by Siegesbeckia orientalis L. grown in Cd-contaminated soils," *Chemosphere*, vol. 91, no. 9, pp. 1362–1367, 2013.

[18] Z. Zou, R. Qiu, W. Zhang et al., "The study of operating variables in soil washing with EDTA," *Environmental Pollution*, vol. 157, no. 1, pp. 229–236, 2009.

[19] M. A. Mohamed, A. Efligenir, J. Husson, J. Persello, P. Fievet, and N. Fatin-Rouge, "Extraction of heavy metals from a contaminated soil by reusing chelating agent solutions," *Journal of Environmental Chemical Engineering*, vol. 1, no. 3, pp. 363–368, 2013.

[20] B. Serpaud, R. Al-Shukry, M. Casteignau, and G. Matejka, "Adsorption des métaux lourds (Cu, Zn, Cd et Pb) par les sédiments superficiels d'un cours d'eau: rôle du pH, de la température et de la composition du sédiment," *Revue des Sciences de l'eau*, vol. 7, p. 343, 1994.

[21] L. Citeau, F. Gaboriaud, F. Elsass, F. Thomas, and I. Lamy, "Investigation of physico-chemical features of soil colloidal suspensions," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 287, no. 1–3, pp. 94–105, 2006.

[22] D. Hristozov, C. E. Domini, V. Kmetov, V. Stefanova, D. Georgieva, and A. Canals, "Direct ultrasound-assisted extraction of heavy metals from sewage sludge samples for ICP-OES analysis," *Analytica Chimica Acta*, vol. 516, no. 1-2, pp. 187–196, 2004.

[23] Z. Ding, Q. Wang, and X. Hu, "Extraction of heavy metals from water-stable soil aggregates using EDTA," *Procedia Environmental Sciences*, vol. 18, pp. 679–685, 2013.

[24] Z. Hseu, Z. Chen, T. Tsai et al., "Digestion methods for total heavy metals in sediments and soils," *Water, Air, & Soil Pollution*, vol. 141, pp. 189–205, 2002.

[25] Y. Lu, F. Zhu, J. Chen, H. Gan, and Y. Guo, "Chemical fractionation of heavy metals in urban soils of Guangzhou, China," *Environmental Monitoring and Assessment*, vol. 134, no. 1-3, pp. 429–439, 2007.

[26] V. Ivezić, Z. Lončarić, M. Engler, D. Kerovec, and B. R. Singh, "Comparison of different extraction methods representing available and total concentrations of Cd, Cu, Fe, Mn and Zn in soil," *Poljo Privreda*, vol. 19, pp. 53–58, 2013.

[27] C. E. Renn, "Biodegradtion of NTA detergents in a wastewater treatment system," *Journal of the Water Pollution Control Federation*, vol. 46, pp. 2363–2371, 1974.

[28] J. L. Means, T. Kucak, and D. A. Crerar, "Relative degradation rates of NTA, EDTA and DTPA and environmental implications," *Environmental Pollution Series B, Chemical and Physical*, vol. 1, no. 1, pp. 45–60, 1980.

[29] A. L. Rufus, S. Velmurugan, V. S. Sathyaseelan, and S. V. Narasimhan, "Comparative study of nitrilo triacetic acid (NTA) and EDTA as formulation constituents for the chemical decontamination of primary coolant systems of nuclear power plants," *Progress in Nuclear Energy*, vol. 44, no. 1, pp. 13–31, 2004.

[30] B. Sun, F. J. Zhao, E. Lombi, and S. P. McGrath, "Leaching of heavy metals from contaminated soils using EDTA," *Environmental Pollution*, vol. 113, no. 2, pp. 111–120, 2001.

[31] H. Ciesielski, A. Guérin-Lebourg, and N. Proix, "Effets du pH sur l'extraction des éléments traces métalliques dans les sols," *Revue Étude et Gestion des Sols*, vol. 14, pp. 7–30, 2007.

[32] C. Zhang, Z.-G. Yu, G.-M. Zeng et al., "Effects of sediment geochemical properties on heavy metal bioavailability," *Environment International*, vol. 73, pp. 270–281, 2014.

[33] K. Ennaciri, A. Baçaoui, M. Sergent, and A. Yaacoubi, "Application of fractional factorial and Doehlert designs for optimizing the preparation of activated carbons from Argan shells," *Chemometrics and Intelligent Laboratory Systems*, vol. 139, pp. 48–57, 2014.

[34] J. Goupy, "Manuel d'utilisation du logiciel JMP (VERSION 9) Plans d'expériences," 2009, http://jacques.goupy.pagespersoorange.fr/Manuel_JMP_V9_1.pdf.

[35] M. Ematiques, *Plans d'expérience: constructions et analyses statistiques*, Vol. 67, Springer Berlin Heidelberg, Heidelberg, Germany, 2010.

[36] *La législation wallonne sur les sols*, http://www.environnement-entreprise.be/sites/uwe-environnement/files/Docs/outils/sol-ds_decret_sols_2017.pdf, 2009.

[37] T. Deschamps, M. Benzaazoua, B. Bussière, T. Belem, and M. Mbonimpa, "Mécanismes de rétention des métaux lourds en phase solide : cas de la stabilisation des sols contaminés et des déchets industriels," *VertigO*, vol. 7, 2006.

[38] P. Moszkowicz, "Caractérisation de la mobilisation de polluants inorganiques présents dans les sols pollués," in *Etude N° 00-0505/2A*, Record, Laepsi, Insa Lyon, Villeurbanne, France, 2002.

[39] M. T. Beck, "Critical evaluation of equilibrium constants in solution: stability constants of metal complexes," *Pure and Applied Chemistry*, vol. 49, no. 1, pp. 127–136, 1977.

[40] E. R. Souaya, E. H. Ismail, and N. E. Milad, "Determination of acid dissociation and stability constants of 1:1 and 1:2 complexes of acid chromium and lanthanon nitrilotriacetates," *American-Eurasian Journal of Scientific Research*, vol. 1, no. 1, pp. 49–51, 2006.

[41] D. Koodynska, "Chelating agents of a new generation as an alternative to conventional chelators for heavy metal ions removal from different waste waters," in *Expanding Issues in Desalination*, IntechOpen, Rijeka, Croatia, 2011.

[42] J. Labanowski, F. Monna, A. Bermond et al., "Kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil: EDTA vs. citrate," *Environmental Pollution*, vol. 152, no. 3, pp. 693–701, 2008.

[43] F. A. Smith, "Determination of NTA and EDTA and speciation of their metal complexes in aqueous solution by capillary electrophoresis," *Environmental Science & Technology*, vol. 34, no. 5, pp. 885–891, 2000.

[44] M. D. Andrade, S. O. Prasher, and W. H. Hendershot, "Optimizing the molarity of a EDTA washing solution for saturated-soil remediation of trace metal contaminated soils," *Environmental Pollution*, vol. 147, no. 3, pp. 781–790, 2007.

[45] I. Mohamed, B. Ahamadou, M. Li, C. Gong, P. Cai, and W. Liang, "Fractionation of copper and cadmium and their binding with soil organic matter in a contaminated soil amended with organic materials," *Journal of Soils and Sediments*, vol. 10, no. 6, pp. 973–982, 2010.

[46] B. Mohanty and A. B. Mahindrakar, "Removal of heavy metal by screening followed by soil washing from contaminated soil," *International Journal of Technology And Engineering System*, vol. 2, pp. 290–293, 2011.

[47] T. A. Kirpichtchikova, A. Manceau, L. Spadini, F. Panfili, M. A. Marcus, and T. Jacquet, "Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling," *Geochimica et Cosmochimica Acta*, vol. 70, no. 9, pp. 2163–2190, 2006.

[48] K. Wiatrowska and J. Komisarek, "Role of the light fraction of soil organic matter in trace elements binding," *PLoS One*, vol. 14, no. 5, Article ID e0217077, 2019.